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ENHANCING TENSILE RESPONSE OF Sn USING Cu AT NANO LENGTH SCALE AND HIGH TEMPERATURE EXTRUSION

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Abstract

In the present study, 1.1 volume percent of nano size copper was incorporated into pure tin using hybrid microwave sintering assisted powder metallurgy route. Microwave sintered samples were extruded both at room temperature and at 230 °C. Microstructural characterization studies were conducted on the extruded samples to investigate the distribution characteristics of secondary phase and grain morphology. Room temperature tensile test results revealed that hot extruded Sn-Cu samples exhibited higher strengths (~ 41%, in case of 0.2% yield strength and ~ 38%, in case of ultimate tensile strength) and ductility (~ 15%) when compared to room temperature extruded samples. On the contrary, the tensile properties of pure tin remained independent of extrusion temperature. An attempt is made in this study to correlate the effect of extrusion temperature on the microstructural evolution and tensile properties of Sn-Cu solder.

Introduction

Tin is mostly used as a main element of solder materials in electronic packaging industries. Traditionally, conventional eutectic Sn-37Pb solders have been widely used throughout the electronic packaging industries since they have a low melting point, low cost and good wettability [1]. However, environmental concerns over the use of toxic Pb have led to the ban of its uses in electronics manufacturing by USA, Japan and the countries under European Union. This development has paved the way for the usage of Sn in new lead-free solders exceeding 95%. Among the new lead-free solders, Sn-3.5 wt. % Ag, Sn-3.0 wt. % Ag-0.5 wt. % Cu and Sn-0.7 wt. % Cu are most commonly used. Solder manufacturers are actively looking into lead-free solders that do not contain silver to reduce the material's cost as the cost of silver has increased significantly in recent times, making Sn-Cu formulations an obvious choice. However, mechanical strength of Sn-0.7 wt. % Cu solder synthesized using equilibrium solidification processes is relatively low when compared to the Sn-Pb or Sn-Ag-Cu system and this may lead to reliability issues [2]. With increasing miniaturization and more input/output terminals, it is becoming increasingly important to develop new interconnect materials with enhanced mechanical properties to realize similar or enhanced reliability when compared to Sn-Pb solder.

One way of improving the properties of the solder is the judicious selection and innovation of the processing techniques [3-4]. Powder metallurgy (PM) technique is one of the obvious choices to produce high performance metallic materials for various applications as it offers advantages like near-net shaping, greater materials utilization and more refined microstructure [3]. Sintering is an important step where densification and bond formation takes place and is traditionally carried out using conventional resistance furnaces [5-6]. However, recent investigations have shown that microwaves can be utilized to sinter powder compacts much more rapidly than conventional sintering, producing materials with better microstructural and mechanical properties [2, 4, 7].

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14. ABSTRACT
In the present study, 1.1 volume percent of nano size copper was incorporated into pure tin using hybrid microwave sintering assisted powder metallurgy route. Microwave sintered samples were extruded both at room temperature and at 230 ?C. Microstructural characterization studies were conducted on the extruded samples to investigate the distribution characteristics of secondary phase and grain morphology. Room temperature tensile test results revealed that hot extruded Sn-Cu samples exhibited higher strengths (~ 41%, in case of 0.2% yield strength and ~ 38%, in case of ultimate tensile strength) and ductility (~ 15%) when compared to room temperature extruded samples. On the contrary, the tensile properties of pure tin remained independent of extrusion temperature. An attempt is made in this study to correlate the effect of extrusion temperature on the microstructural evolution and tensile properties of Sn-Cu solder.

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Extrusion temperature also has a strong influence on the microstructural and mechanical response of the materials [8-11]. However, the results of open literature search indicate that no research attempt is made so far to synthesize Sn and Sn-1.1Cu solder containing nano length Cu using microwave sintering assisted powder metallurgy route and to investigate their tensile behavior at different extrusion temperatures.

Accordingly, in the present study, pure Sn and Sn-1.1 vol. % Cu solder were synthesized by adding nano-size copper particles using powder metallurgy method incorporating microwave sintering and at different extrusion temperature. Particular emphasis is placed in the present study to correlate the effect of extrusion temperature on the microstructural evolution and tensile properties of Sn-Cu solder.

Experimental Procedure

Materials

In the present study, air atomized pure tin powder, which had a nodular to teardrop particle shape with -325 mesh size (less than 44 μm) of 99.9% purity (supplied by NOAH Technologies Corporation, Texas, USA) was used as matrix material and copper nanopowder of 99.8% purity with an average particle size of 25 nm (supplied by Nanostructured and Amorphous Materials, Los Alamos, USA) was used as the reinforcement phase.

Primary Processing

The powder metallurgy technique was used to synthesize pure tin and Sn-1.1Cu (by vol. %) solder in this study. Pure tin powder and copper nano powder were weighed carefully in an argon filled glove box (containing less than 0.1 ppm of oxygen) and blended in a RETSCH PM-400 mechanical alloying machine using a speed of 200 rpm for 1 hour. The blended powders were compacted to 40 mm height and 35 mm diameter preforms by hydraulic compaction at a pressure of 510 MPa (~50 tonne) using a 150 tonne press. The preforms were coated with colloidal graphite and sintered using microwave assisted hybrid sintering technique for 11 min and 24 seconds to 226 °C in a 900 W, 2.45 GHz SHARP microwave oven using SiC as the microwave susceptor material [2, 4, 7].

Secondary Processing

Sintered preforms were extruded both at room temperature and high temperature using an extrusion ratio of 26.5: 1 on a 150 tonne hydraulic press. High temperature extrusion was carried out at 230°C. The preforms were soaked at 230°C for 5 minutes before extrusion. Rods of 7 mm diameter were obtained following extrusion.

Density Measurement

Density measurements were performed in accordance with Archimedes' principle on four randomly selected polished samples taken from each extruded rods [4]. Distilled water was used as the immersion fluid. The samples were weighed using an A&D HM-202 electronic balance with an accuracy of ± 0.00001 g.

Microstructural Characterization

Microstructural characterization studies were performed on metallographically polished extruded samples to investigate morphological characteristics of grains, pores and intermetallic compounds. The etching solution was made by mixing 5 vol. % HCl in ethanol to reveal the grain boundaries for microstructural analysis. Hitachi S4300 Field Emission Scanning Electron Microscope (FESEM) equipped with Energy Dispersive Spectroscopy (EDS) was used. Image analysis using the Scion system was carried out to quantify the microstructural features. The inter-particle spacing (λ) was estimated using the following equation [12]:

$$\lambda \approx d_p \left[\left(\frac{\pi}{4V_p} \right)^{\frac{1}{2}} - 1 \right] \quad (1)$$

where d_p is the size of particle and V_p is the volume fraction of particles.

X-Ray Diffraction

An automated Shimadzu LAB-X XRD-6000 diffractometer was used for the phase analysis of extruded samples. The samples were polished and exposed to Cu Kα radiation (λ = 1.54056 Å) using a scanning speed of 2 deg/min. In addition, a scanning speed of 0.2 deg/min was also used on Sn-1.1Cu sample to have more counts to facilitate the identification of second phases. The Bragg angle and the values of the interplanar spacing, d, obtained were subsequently matched with the standard values for Sn, Cu and other related phases.

Tensile Testing

The smooth bar tensile properties of the extruded pure tin and Sn-Cu samples were determined in accordance with ASTM test method E8M-01 using MTS 810 tensile testing machine with a crosshead speed set at 0.254 mm/min on round tension test specimens of 5 mm diameter and 25 mm gauge length.

Results and Discussion

Macrostructure

The result of macrostructural characterization conducted on sintered and extruded samples did not reveal presence of macropores, cracks or any other defects. The results suggest the appropriateness of processing parameters and methodology used in the present study.

Density Measurement

The results of the density measurements on the room and high temperature extruded samples are shown in Table I. Results revealed that relatively higher density was realized for high temperature extruded samples when compared to room temperature extruded samples. This can be attributed to the higher extrusion temperature that lead to higher diffusion rates leading to decreased porosity [8].

Table I. Results of Density and Characteristics of Grains and Pores

Materials	Volume % of Cu	Density[a] ρ_{ex} (g/cc)	Grain Characteristics[b]		Pores Characteristics[c]	
			Size (μm)	Aspect Ratio	Size (nm)	Aspect Ratio
Sn/RTX	-	7.180 ± 0.01	2.5 ± 0.8	1.5 ± 0.4	140 ± 101	2.0 ± 1.0
Sn/HTX	-	7.252 ± 0.03	3.7 ± 1.3	1.5 ± 0.4	144 ± 78	1.7 ± 0.6
Sn-1.1Cu/RTX	1.1	7.225 ± 0.01	1.7 ± 0.7	1.6 ± 0.5	156 ± 72	2.8 ± 1.2
Sn-1.1Cu/HTX	1.1	7.235 ± 0.01	2.3 ± 0.7	1.5 ± 0.3	114 ± 57	1.7 ± 0.5

RTX= Room Temperature Extrusion; HTX= High Temperature Extrusion.
[a] Four samples from each specimen were tested.
[b] More than 100 grains were taken into consideration.
[c] More than 50 pores were taken into consideration.

Microstructural Characterization

Results of microstructural characterization of extruded samples are shown in Tables I and II and in Figures 1 to 3 and discussed in terms of: (a) grain morphology, (b) pore morphology and (c) the presence, distribution and morphology of the second phase particles. The microstructural characterization results revealed the presence of near-equiaxed grains for all samples indicating its independency on the incorporation of nano length Cu particles and/or the extrusion temperature (see Table I). Larger average grain size was observed for high temperature extruded Sn and Sn-1.1Cu samples (see Table I and Figure 1). This can be attributed to the additional energy that was provided during high temperature extrusion. Furthermore, average grain size decreases with the copper addition. This can be attributed to the pinning of grain boundaries by the second phases resulting in limited grain growth.

Table II. Results of Secondary Phase Characteristics and XRD of Sn and Sn-1.1Cu Solders

Materials	Secondary Phase Characteristics[a]				XRD[b]		
	Size (μm)	Aspect Ratio	Vol. %	λ (μm)	Sn	Cu	Cu_6Sn_5
Sn/RTX	-	-	-	-	9[3]	-	-
Sn/HTX	-	-	-	-	9[3]	-	-
Sn-1.1Cu/RTX	0.9 ± 0.8	2.0 ± 0.8	2.68	4.0	10[3]	-	1
Sn-1.1Cu/HTX	1.1 ± 0.5	1.6 ± 0.6	3.23	3.1	10[3]	-	1

[a] A minimum of 50 secondary phase were quantified in each case.
[b] Numbers in square brackets indicate the number of main peaks matched.

Table I and Figure 2 shows the pore morphology of pure tin and Sn-1.1Cu samples both for room temperature and high temperature extrusion conditions. Lowest average pore size was observed for hot extruded Sn-1.1Cu samples. However, considering standard deviation, variation of pore size is statistically insignificant and can be said to be independent of extrusion parameter or incorporation of Cu particles. Sharper pores (high aspect ratio) were observed in room temperature extruded samples when compared to the high temperature extruded samples. Highest average aspect ratio of pores (2.8) was exhibited by room temperature extruded Sn-1.1Cu

samples suggesting the presence of lenticular pores. This aspect ratio of pores was only 1.7 for high temperature Sn-1.1Cu samples. This can be attributed to the higher extrusion temperature that provides easier flow of the matrix alloys under applied shear forces resulting in filling the voids or breaking the lenticular pores into small pores besides higher atomic diffusion rates [8].

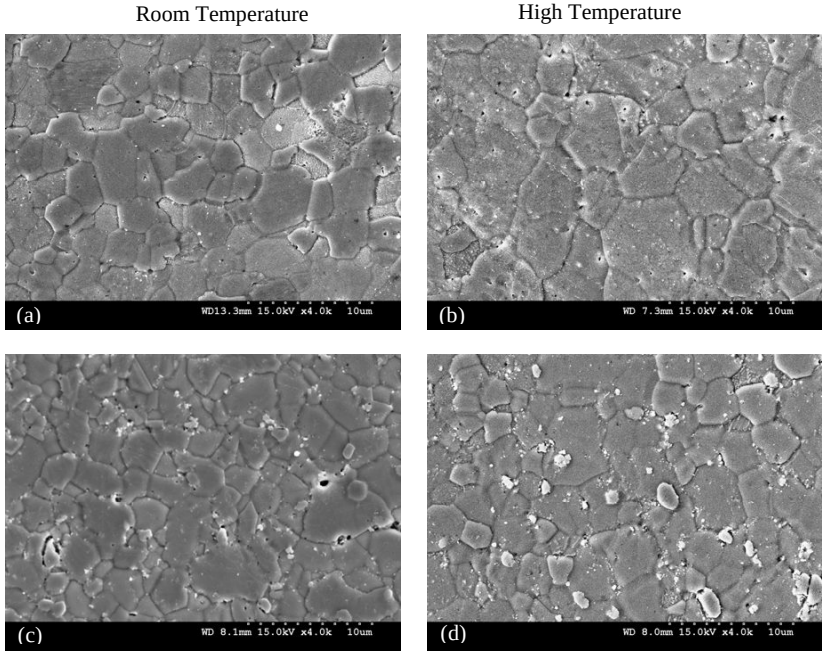

Figure 1. Representative FESEM micrographs showing the grain morphology of: (a) room temperature and (b) high temperature extruded Sn samples. Figures (c) and (d) show the grain morphology of room temperature and high temperature extruded Sn-1.1Cu samples respectively.

The morphology of secondary phase is shown in Table II and Figure 3. Relatively larger and more uniform distribution of second phase particles was observed in high temperature extruded Sn-1.1Cu samples. Sn-1.1Cu room temperature extruded samples showed higher evidences of cluster formation. The applied shear stress during high temperature extrusion assisted in breaking up these clusters resulting in a more uniform particle distribution [8]. Volume percent of second phase also increased for high temperature extruded samples. This may be attributed to the further reaction between partly unreacted Cu particles in Sn-1.1Cu samples with tin during high temperature extrusion leading to the formation of Sn-Cu second phase. Furthermore, hot extruded Sn-1.1Cu samples exhibited lower inter-particle spacing (λ) (see Table II). This can be attributed to the presence of higher volume fraction of second phase that reduces the inter-particle spacing.

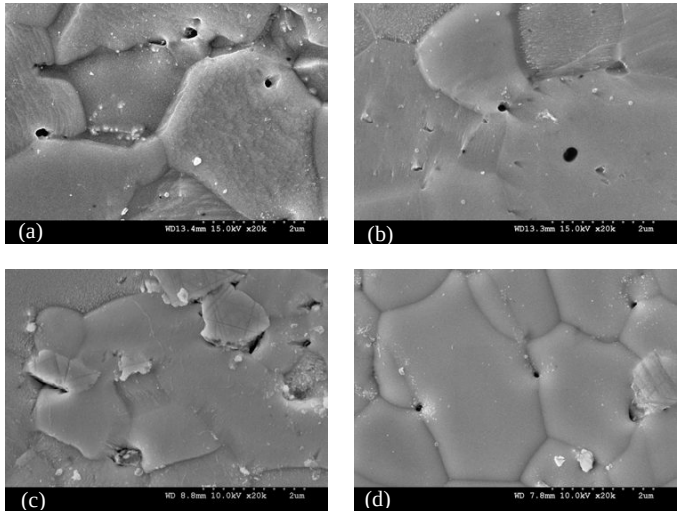

Figure 2. Representative FESEM micrographs showing the pore morphology of (a) Sn and (c) Sn-1.1 Cu samples extruded at room temperature and (b)Sn and (d) Sn-1.1Cu samples extruded at high temperature respectively.

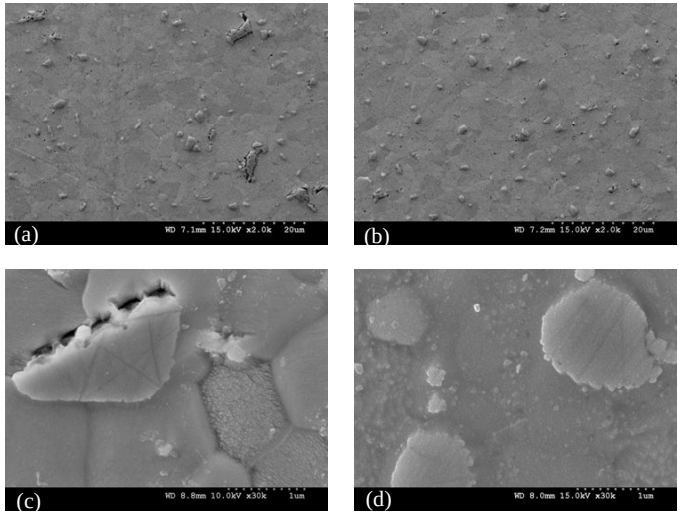

Figure 3. Representative FESEM micrograph showing the second phase distribution of Sn-1.1Cu for (a) room temperature and (b) high temperature extruded samples. Figures (c) and (d) showing the interfacial bonding of IMC for room and high temperature extruded samples respectively.

X-Ray Diffraction

X-ray diffraction (XRD) was carried out on all samples (see Table 2). Only Sn phase was detected while Cu and Cu related phases were not detected in the Sn-1.1Cu samples for the scan rate of 2.0 deg/min. However, a slow speed scan (0.2 deg/min) conducted on Sn-1.1Cu sample revealed a single peak corresponding to Cu_6Sn_5 (see Table 2). EDS results conducted on the polished samples further confirmed the presence of Sn-Cu phases in Sn-Cu solder samples.

Tensile Testing

The results of ambient temperature tensile tests revealed that considering standard deviation, there is no influence of extrusion temperature on the tensile response of pure Sn (see Table III). Better tensile response was exhibited for hot extruded Sn-1.1Cu samples when compared to room temperature extruded Sn-1.1Cu samples. Hot extruded Sn-Cu samples exhibited ~41% higher 0.2 % yield strength (YS) and ~38% ultimate tensile strength (UTS) when compared to room temperature extruded samples. The increase in 0.2% YS and UTS can be analyzed in terms of morphological characteristics associated with (i) pores and (ii) secondary phases.

Table III. Results of Room Temperature Tensile Properties of Sn and Sn-1.1Cu Solders

Materials	0.2% YS (MPa)	UTS (MPa)	FS (%)	WoF (MJ/m^3)
Sn/RTX	32 ± 3	40 ± 4	10.0 ± 2.2	6.3 ± 1.6
Sn/HTX	35 ± 2	39 ± 3	10.0 ± 0.5	6.1 ± 0.7
Sn-1.1Cu/RTX	32 ± 3	37 ± 5	6.2 ± 0.3	3.4 ± 0.5
Sn-1.1Cu/HTX	45± 0	51 ± 3	7.1 ± 0.3	5.9 ± 0.3

RTX= Room Temperature Extrusion; HTX= High Temperature Extrusion.

Result of pore morphology shows that aspect ratio significantly decreases from 2.8 to 1.7 when the Sn-Cu samples extruded at higher temperature (see Table I and Figure 2). This means relatively round pores were observed for hot extruded Sn-Cu samples that helps to increase the strength. The lenticular pores (higher aspect ratio) in room temperature extruded Sn-1.1 Cu samples can act as stress concentration sites leading to premature failure (see Tables 1 and 3 and Figure 2) [4]. Increment of 0.2% YS and UTS for hot extruded Sn-Cu solder can also be attributed to the formation and the increasing presence of intermetallic phase in the matrix (see Tables II and III and Figure 3). The non-reacted copper particles might be reacted with pure tin during high temperature extrusion to form relatively higher volume percent of intermetallic compounds and modified the microstructural features, hence increasing strength. Smaller inter-particle spacing is also a strengthening mechanism in this study (see Table II). The smaller inter-particle spacing leads to higher material's strength as the passage of dislocations through the second phase particles will require higher stresses [13]. On the other hand, higher aspect ratio of the second phase for room temperature extruded samples act as a stress concentration site that causes premature failure (see Table II) [2]. The poor interfacial bonding between second-phase and matrix is yet another parameter found in this study that led to lower strength and failure strain of room temperature extruded Sn-Cu samples (see Figure 3).

Table III shows that the failure strain (FS) and work of fracture (WoF) decreases with incorporation of Cu when compared to pure tin. This can be attributed to the presence of relatively harder second phase that serves as crack nucleation sites, resulting in a decrease in FS under tensile loading condition. This observation is consistent with the findings of other

researchers working in other solder materials [14-15]. Among the Sn-Cu samples, hot extruded samples exhibited ~15 % higher FS and ~74% higher WoF when compared to room temperature extruded samples (see Table III). This can be attributed to the presence of relatively round pore (instead of lenticular pore for room temperature extruded samples), rounder intermetallics and better interfacial bonding between second phase and matrix when compared to room temperature extruded Sn-Cu samples (see Figure 3).

Conclusions

The following conclusions can be made from the present study:

1. Pure Sn and Sn-1.1Cu solder can be successfully synthesized using microwave sintering assisted powder metallurgy route.
2. Relatively high density and better microstructural properties can be obtained by extruding Sn-Cu samples at higher temperature.
3. Best overall tensile properties (in terms of 0.2% YS and UTS) were observed for hot extruded Sn-1.1Cu solder.

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